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- POLAND -

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SEPARATION OF ISOTOPES IN AN ULTRACENTRIFUGE

— POLAND —

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Problems of separation of isotopes in an ultracentrifuge are discussed. Basic design features of recent ultracentrifuges are described. Essential elements of the theory of isotope separation in an ultracentrifuge are outlined. Experimental results are reviewed.

I.

Theoretical work on isotope separation by means of pressure gradient, and so employing rotation, were undertaken in the early 1920's by Lindemann and Aston (1) and Chapman (2), who investigated such operation in a way parallel to that of isotope separation by means of temperature gradient. Further theoretical developments are to be found in the works by Mulliken (3, 4, 5) and by Harkins (6), published a few years later.

First theoretical works concerned the problems connected with the simple isotopic effect of separation. Among other matters, they stated the definition of the coefficient of isotopic mixture, and its dependence upon the parameters, stressing the most important advantage of centrifugation, namely, the relative /see note/ independence of its results of the molecular weight of the components of the isotopic mixture, now undergoing separation. They pointed to certain analogies between centrifugation and thermal diffusion. (Note: Among other factors, the course of the operation depends upon the coefficients of the diffusion of mixture components which, in turn, depends upon /their/ molecular weight.)

Along with theoretical work, practical experiments were undertaken at almost the same time. They were stimulated by the earlier discoveries of radioactive chains of uranium and of thorium, and of the phenomenon of isotopy of lead.

Joly and Poole (7) attempted to separate lead isotopes in a 40 mm diameter centrifuge, 60 mm long, with a rotational velocity of 9,000 r.p.m. While the attempts by these authors to separate alloys were promising, the effects of isotopic separation were too insignificant of the order of an error in determining density. A similar case was that of the separation of mercury isotopes (8) after they had been

discovered by Aston. The anticipated increase in the density of mercury on the periphery of the centrifuge by 0.00003 was too slight to be measured accurately, using the densimetric methods of the period.

The failure of the attempts to separate isotopes was, first of all, attributed to centrifuge vibrations, and to the eneven distribution of temperature, causing convection currents and the mixing of the isotopic mixture undergoing separation. However, Pollock (10) reached the conclusion that due to low velocity of diffusion in liquids, the attempts at separating liquid isotopic mixtures showed little primise even in fields where the tension of the centrifugal force was equal to 500,000 g, and even when the effects of vibration and of convection might be neglected. Therefore, all subsequent attempts undertaken for the purpose of separating isotopes in centrifuge concerned gas or vapor mixtures, placed in the centrifuge through the introduction in (its) rotor of a small amount of liquid whose vapor was highly resilient.

The unsuccessful attempts at separating isotopes in the technically crude centrifuges of the period checked the progress of the pertinent experiments for a long time. They were resumed no earlier than the late 1930's, when thanks to the efforts of a number of researchers and designers the centrifuges attained a high level of perfection.

II.

The experiments concerning the separation of isotopes in the field of centrifugal force were most closely connected with the technical possibilities of the centrifuge. Therefore, it is worth while to cast a glance, however cursory, at the most important developments in this respect.

The design of high rotational speed centrifuges, or so-called ultracentrifuges, followed the lines of increasing the rotational speed, of eliminating the vibration and the precessional motion of the rotor, and of removing the sources of temperature gradients appearing in the rotor chamber. Here, two development trends may be distinguished, as represented by Svedberg and by Beams, the two most outstanding researcher-designers in this field:

Svedberg's cyclical ultracentrifuges were, first and foremost, meant for research into sedimentation, and for the determination of the molecular weights of macromolecular compounds. Therefore, no detailed description will be attempted, and it will only be mentioned that some of the, such as centrifuges with 32.5 mm rotor diameter, hydrogen-cooled under (hydrogen) pressure of 20 mm Hg, reached speeds of 710,000 r.p.m. while at usual work. The tension of the centrifugal force field went up to 900,000 g. Rotational speed was limited not so much by kinematic features as by the (limits to) the tensile strength of the material (chrome-nickel alloy) of which the rotor was made. In the case under discussion, the rotor was coupled with a small turbine, driven by a stream of oil.

In their designs, Beams (13) and a number of other designers (14, 15, 16) followed the lines of developing and improving the "air-top" as built by Henriot and Huguenard (17, 18).

The "air-top" is a conical rotor with radiating grooves in the tapering face, located in a funnel-like stand, whose apical angle is slightly wider than that of the rotor. There are air ducts in the stand, and their exits, equidistant from the apex, are tangent to the circle traced by them. Compressed air, escaping through the exits, sets the rotor of the air-top spinning. The drop in pressure, originating in the chink between the rotor and its stand, does not allow the rotor to be "blown" off its bearing. Between the rotor and its stand, a layer of evenly distributed air appears which plays the part of a sliding insert of the bearing. Therefore, it can be said that the ultracentrifuge based on the "air-top" principle is air-supported.

The design of such centrifuge was brought by Beams to a high degree of perfection. The rotor of one of them (also used for measuring and demonstrating the speed of light), 9 mm in diameter, driven by hydrogen under 11 atm. pressure, reached the speed of 1, 300,000 r.p.m. (13, 19, 20).

The insufficient tensile strength of materials (high grade steel, Duralumin alloys) of which rotors were made constituted an obstacle to the use of such rotational velocities for purposes of isotope separation. When used for such purposes, rotors must be much larger than the one described above. The rotor of an ultracentrifuge used for isotope separation must have a minimum capacity that would make it possible to obtain a convenient amount of material both for analytical determination and for further experiments with enriched isotopes. Increasing the rotor diameter at a limited tensile strength of the material used brings about the need for decreasing the rotational speed of the ultracentrifuge. These circumstances, in addition to others, led to the conclusion that an elongated cylinder was the most rational shape for an ultracentrifuge rotor used for the separation of isotopic mixtures. The diameter being relatively small -- as a rule 5 to 15 cm -- the capacity of the rotor chamber may be considerable as there are no reasons -- so far -- pointing to the need for limiting its length (21, 22, 24).

The following paragraphs briefly describe the ultracentrifuges which, after a lengthy interval, were used in the resumed attempts at separating isotopes (24 to 29). Their description shows the remarkable progress meanwhile achieved in this respect.

In the attempts to separate isotopes undertaken in the late 1930's, a rotor was generally used, suspended from a flexible steel capillary, a few millimeters in diameter, coupled with the axis of the rotor of the air turbine built in accordance with the "air-top" principle. The rotor was located in a vacuum chamber, made airproof by means of a system of oil baffles. The vacuum obtained in the chamber -- of the order of 10^{-5} to 10^{-7} mm Hg -- was limited by the resilience of the oil vapor in the baffles. The use made of the vacuum chamber removed the motor-air friction that used to raise its temperature, and made it possible to maintain

an even temperature in particular portions of the rotor, and to carry out the operation, if need be, within a rather wide range of temperatures; this circumstance evidently enhanced the experimental advantages offered by the device. The team of turbine-and-centrifuge constituted a self-weighing system. Therefore, the need disappeared for the painstaking, extremely thorough procedures of weighing the rotating parts as to both their statics and dynamics. Not only did the compressed air set the turbine in motion but, when conveniently directed, it slightly raised the turbine rotor together with the centrifuge coupled therewith, thus to a great extent compensating the weight of the system, reaching 12 k. Vibration appeared in a transitory way while the device was being set in motion, within a determined and rather sharply outlined range of the critical rotational speed. Beyond that range, even the microscope failed to detect any vibration.

As was said, the mechanical tensile strength of the construction materials was the only factor limiting the rotational speed. Thus, for instance, a 100 mm rotor made of ST/4 Duralumin was torn apart at 1,650 r.p.sec. Therefore, 1,550 r.p.sec. was used as working speed. At such speed, the centrifuge worked for 700 hours without sustaining any damage.

The capillary from which the rotor was suspended was used for filling the centrifuge with liquid or gas, and for receiving gas or vapor particles coming from the rotor. Using for coupling two capillaries on the same axis, it was possible to perform the operation uninterruptedly.

In addition to air propulsion which requires a 400 to 800 min compressor at a pressure of 6 to 8 atm, vapor propulsion was also used (19, 30). This, however, complicated the structure of the rotor as it required a very thorough thermal insulation of the vapor ducts leading from the vacuum chamber.

Electric propulsion, by both synchronous and asynchronous low-power motors, was also used (31, 32). Alternate high-frequency current was obtained by transforming industrial a.c. by means of a convenient oscillating system, in which electronic tubes were used.

At the outset, air bearings were used as well in the current-driven ultracentrifuge. However, the use became more and more widespread of the method of suspending the rotating part in the magnetic field of one or of several solenoids (32 to 37). A centrifuge suspended without any mechanical contraptions being used can be rotated by an external rotating magnetic field (38). Such rotors can easily attain 180,000 r.p.m.; any further increase in rotational speed depends on the tensile strength of the materials employed.

A few years ago, Beams described the centrifuge he had built (35, 36): Its weight amounted to about 5 k, diameter - -130 mm; it was suspended in the magnetic field of a 28,000-coil solenoid, 1,200 ohms resistance, own inductivity equal to 70 H. The intake of current; 150 to 220 m. The rotor was steered by means of an electronic system through a small induction tube located underneath the rotor. When the steering circuit was conveniently adjusted, the microscopic observation

of the rotor failed to detect any vibrations. The rotor was set spinning by means of an air turbine. After a suitable speed had been reached, the propellant was switched off. Due to minimum friction, the retardation caused thereby was equal to 0.1 r.p.sec. within one hour.

Recently, there was news of methods of adjusting centrifuges for work in high (above 500°C) temperatures. Even without taking the design requirements into consideration, one should probably not anticipate their being employed in the operations aimed at separating isotopic mixtures owing to the lower separation coefficient in high temperatures:

$$(a_o \quad \exp. \frac{1}{T}).$$

At this juncture, it is perhaps worthwhile to note the rather puzzling circumstance that in a number of the works on isotopic separation in a centrifuge (these will be referred to below) published over the past decade there is no direct information concerning the use being made of Beams' design relative to the propulsion and seating of ultracentrifuges. The writers confine themselves, in principle, to very moderate rotational speeds of the order of 40,000 to 50,000 r.p.m. These researchers try to increase the effectiveness of separation by means of various inserts in the rotor which -- according to them -- bring about the emergence of hydrodynamic conditions inside the rotor, such conditions being more advantageous for separating mixtures. Among others, there are horizontal inserts, aimed at checking the convection currents which cause the mixing of gas, and perpendicular, angle partitions which ensure an even angular velocity of the entire mass of rotated gas.

Certain researchers attribute a great importance to convection currents flowing in radial directions. According to Beams' forecast (20), and to the theoretical reasoning of Martin (48), the radial convection currents, awakened in an ultracentrifuge under conditions of great stress of the centrifugal force from the local T temperature gradients, differ vastly from the ordinary convection currents which for identical reasons appear in the earth's weak gravitational field. Already at momentum of the order of 120,000 to 150,000 g, corresponding to rotational speeds of 40,000 to 45,000 r.p.m. in a 130 mm diameter centrifuge, the pressures from 100 molecular weight gas inside the rotor and on its periphery form a relation equal to 7.5 : 1. At the molecular weight of gas being equal to 200, this relation rises to 56 : 1, and at 300 amounts to 414 : 1. Due to this considerable difference in pressures, the radial convection flow is connected with appreciable effects of compression and of decompression which, in turn, cause serious local changes in temperature.

The problem is not altogether clear. There are a number of contradictory opinions on the influence of thermal convection currents in an ultracentrifuge upon the course of separation. Some believe the thermal convection currents to be the reason of the gas mixing, thus diminishing the effects of separation (42, 40, 41). Others are inclined to

attribute to them the emergence of a countercurrent in the rotor, and that, connected with it, of a coefficient of isotopic mixture separation higher than expected of a simple isotopic effect. Moreover, the mixing would be caused by the fact that certain optimum values of convection flow had been exceeded. Up to the present, experimental results have failed to provide a basis for an exact and clear-cut explanation of this problem.

The measuring of the rotational speed of the ultracentrifuge is very important for purposes of quantitative interpretation of experimental results. The rotational speeds up to about 40,000 r.p.m. can be measured by means of mechanical counters. Higher speeds, in particular when the rotor is slightly inert, must be measured by means of stroboscopic systems or of photo cells coupled with oscillographic circuits.

Apart from the description of original works, a great deal of more detailed information concerning the development of design in the construction of ultracentrifuges can be found in the reports by Beams (20) and Kofman (49), still valid in many respects.

III.

On several occasions, a series of works dealt with the theoretical problems concerning the separation of isotopes in a centrifuge. The subject became interesting at the very beginning because of the preliminary assertions and the optimistic suggestions connected with the nature of the coefficient of separation, as contained in the first works, referred to at the outset (1).

Works by Chapman (2), Harkins (6) and Mulliken (2, 4, 5), in the early 1920's contributed to a great extent to the formulation of problems, and pointed to a series of analogies arising in the centrifugation and thermal-diffusion operations.

Some of these works, such as those by Mulliken, in addition to clearness of formulation and argumentation show the prospects for the method of separating isotopes by means of rotational speed. These prospects Mulliken saw in the method of centrifuging vapors originating in the rotor due to the evaporation of a small amount of liquid. While rotating, certain amounts of vapor are being sucked away from the rotor in either a cyclical or a steady manner. By analogy with differential distillation, this method could be called differential rotation. An extreme case of such operation, namely, when the loss of vapor by the rotor is so slow that the liquid-vapor equilibrium is not upset, was investigated theoretically by Mulliken.

Mulliken's correct recommendations concerning a higher effectiveness of centrifuging vapors and gases were confirmed several years later by Pollock's calculations, already mentioned above (10).

For several years, the failure of experiments checked theoretical research as well. The latter was resumed only after the construction of modern centrifuges had made it possible for a number of successful

experiments to be carried out. The interest aroused by the separation of isotopes of heavy elements after the chain reaction U^{235} was discovered also proved a powerful incentive for the development of theoretical work.

Using different methods, and following a different mathematical course, Humphreys (29) broadened Mulliken's reasoning, and made it more general. It concerned the differential centrifugation when the equilibrium of the rotated liquid-vapor system is upset by the rapid taking off of the emerging vapor from the system.

Wilson (50) refers to certain fundamental theoretical problems. Bramley (51) drew attention to the possibility of multiple augmentation of the basic effect of separation in a centrifuge, when an artificially aroused countercurrent is used. Martin and Kuhm (52) published a methodical and exhaustive work concerning this problem. The former in an equally detailed way worked out the theoretical problems connected with the flow of gases through fields of high-tension centrifugal force (48). Cohen published (53) a generalized and concise work on the theory of isotope separation in a centrifuge. A few years ago, Verschaffelt (54) published general theoretical cogitations on centrifugation.

Up to now, the theoretical research has been, in principle, fragmentary, and has failed to lead to a possibly comprehensive, methodologically homogeneous theory of the process. Certain important and extensive segments of the problem have yet to be sufficiently confirmed by experiments relative to all their aspects. Nevertheless, on the basis of the theoretical data extant it is possible to calculate and plan a series of phases of the operation with an accuracy adequate for technical problems.

The isotope separation by means of centrifuging can be performed following three principal methods:

The first is a one-stage separation, carried out in one apparatus. It consists of feeding isotopic gas mixture into the centrifuge at one end through one central orifice or through a number of orifices located along two circuits of circles (such two circuits having an axis in common), placed in the axial portion of the centrifuge and on its periphery, and receiving the mixture (taking it off) at the other end through orifices also ar anged along convenient one-axis circuits of circles. While the gas is flowing through the ultracentrifuge, the isotopic mixture tends to establish, on the plane of rotation, an equilibrium determined by the value of the coefficient of separation. As the outcome of such operation, the mixture is split into two fractions, in which the ratio of the concentration of the component being separated is expressed, under optimum conditions, by the coefficient of separation a_o.

The second method concerns an operation which, by analogy with differential distillation, was called differential centrifugation. As mentioned above, it consists of rotating a certain amount of liquid with relatively high-resilience vapor at a given temperature, while a part of the vapor is taken off the rotor either cyclically or steadily. The

enrichment may be more marked than in the first case, and depends upon the ratio of the quantity of the substance taken off to the residual amount in the ultracentrifuge.

The third method is a multiple operation in a simple apparatus, convetion countercurrent -- either natural or artificially created -- being employed. This is the most promising operation for possible practical use in separating uranium isotopes.

Certain problems connected with the simple process have been briefly mentioned before. Let us recall that the coefficient of separation

$$a_o = e^{\frac{(M_2 - M_1)(\omega r)^2}{2\,RT}} \qquad [1]$$

depends exclusively on the difference of molecular weights M_1 and M_2 of the mixture being separated, on the peripheral speed ω of the centrifuge, and on the temperature T. Therefore, the most suitable chemical compounds can be selected for this operation.

Unlike a number of other isotope separation operations, the coefficient of separation can here be accurately and easily calculated for centrifuges with determined design features. For the peripheral speed $8 \cdot 10^4$ cm/sec, the coefficient of separation, in a way dependent upon the differences between molecular weights, and between temperatures, shapes up, according to Beams and Haynes, as in the table below:

Table 1

$M_2 - M_1$	T w °K			
	300	200	80	20
1	1.13	1.21	1.62	6.8
2	1.29	1.47	2.61	47
3	1.47	1.78	4.23	300
4	1.67	2.16	6.90	2000

The simple, concurrent process of isotope separation in a centrifuge is shown by a differential equation which constitutes a particular form of the general equation derived from the differential calculus of flow. According to Cohen (53), the general equation for centrifuging is as follows:

$$p \frac{\partial N}{\partial t} \quad \frac{D_p}{r} \cdot \frac{\partial}{\partial r} \; r \frac{\partial N}{\partial r} \quad \frac{(M_2 - M_1)(\omega r)^2}{RT} N(1 - N) -$$

$$\frac{1}{r} \cdot \frac{\partial}{r} (Npru) - \frac{\partial}{\partial z} (Npw) \quad D \frac{\partial^2}{\partial z^2} (Np) \qquad [2]$$

In a simple concurrent operation, the speed of the flow in a radical direction is equal to zero, and so U 0. In view of the relatively high speed, the influence of back diffusion, shown by $D \frac{\partial^2}{\partial z^2}(Np)$ can be approximately neglected. Therefore, in the case of a stabilized equilibrium, i.e., when $\frac{\partial n}{\partial t} = 0$, where $\Delta A = \frac{M_2 - M_1 \omega^2}{2RT}$, one obtains the differential equation for centrifugation, concerning a simple, concurrent operation:

$$\frac{Dp}{r}\frac{\partial}{\partial r}\left[r\frac{\partial N}{\partial r} + 2\Delta A \cdot r^2 N(1-N)\right] - \frac{\partial}{\partial z}(Npw) = 0 \qquad [3]$$

From this equation, one can derive the maximum separation capacity of the centrifuge per unit of its length:

$$\left(\frac{\partial U}{z}\right)_{max} = 0.41\frac{\pi Dp}{RT}(\ln a_o)^2 \qquad [4]$$

In the case of feeding the centrifuge axially, at one point, one obtains:

$$\left(\frac{\partial U}{z}\right)_{max} = (0.41)^2\frac{2\pi Dp}{RT}(\ln a_o)^2 \qquad [5]$$

and so, as can be seen, the single input is less advantageous than a two-pronged one (two-streamed one).

The following equations show the shifts in the isotopic composition of each stream:

$$Nr_1,z - Nr_2,o = \frac{L_2}{L_1 + L_2}\left[Nr_2,o - Nr_1,o + \Delta A(r_2^2 - r_1^2)N(1-N)\right](1 - e^{-bz}) \qquad [6]$$

and

$$Nr_2,z - Nr_2,o = -\frac{L_2}{L_1 + L_2}\left[Nr_2,o - Nr_1,o + \Delta A(r_2^2 - r_1^2)N(1-N)\right](1 - e^{-bz}) \qquad [7]$$

in which $b = \frac{2\pi Dp}{RT}\cdot\frac{L_1 + L_2}{L_1 L_2}\cdot\frac{1}{\ln\frac{r_2}{r_1}}$

As said before, we are indebted to Mulliken (3, 4) for the first formulation of the case of equilibrium dependent upon an infinitely low speed of taking off with regard to the theory of differential centrifugation. A more general elaboration of the subject for states differing from equilibrium can be found in the work by Humphreys (29).

The differential equation for the operation is derived from the basic equation [2], taking into consideration that in differential centrifugation the axial flow does not occur ($w = 0$), and the shift in the isotopic composition does not depend on the height of the centrifuge z. In this case, and for a determined state, when $\partial N/\partial t = 0$, one obtains

$$\frac{Dp}{r} \cdot \frac{\partial}{\partial r}\left[r\frac{\partial N}{\partial r} + 2\Delta A \cdot r^2 N(1 - N)\right] - \frac{1}{r} \cdot \frac{\partial}{\partial r}(Npru) = 0 \qquad [8]$$

from which, after certain simplifications and alterations, the expression may be drived for the dependence of the isotopic composition from the speed of the outflow:

$$\left(\frac{N}{1 - N}\right)_o = \left(\frac{N}{1 - N}\right)_{r_2} a_o^{\frac{2y}{2y + P}} \qquad [9]$$

in which $P = \frac{P}{RT} 2\pi ruz$ -- molar speed of outflow; $y = 2\pi z \frac{Dp}{RT}$ -- value of the molar diffusion flow.

In his work, humphreys attains the same expression though following a somewhat different course. Humphreys called the exponent in equation [9]; $2y/(2y+P)$ -- the length of distance between the system and the equilibrium caused by the outflow of P. In point of fact, when P is equal to zero, equation [9] takes on the form of:

$$\left(\frac{N}{1 - N}\right)_o = \left(\frac{N}{1 - N}\right)_{r_2} a_o \qquad [10]$$

This is the essential expression for the shift in the isotopic composition at the state of equilibrium.

From the above, it can be seen that in differential centrifugation a', the effective coefficient of isotope separation is smaller than when the system is in a state of equilibrium:

$$\lg a' \quad \frac{2y}{(2y+P)} \quad \lg a_o \qquad [11]$$

As is known, in differential distillation the composition of the residual substance depends on the final volume: original (initial) volume ratio. Also here, an identical relation appears.

The expression for the isotopic composition of the residuum, dependent upon the amount of liquid left in the centrifuge, was obtained by Humphreys by means of the simplifying premise: $a' \approx 1$. It has the form of a simplified Rayleigh equation:

$$\left(\frac{N}{1 - N}\right)_V = \left(\frac{N}{1 - N}\right)_{V_o} \left(\frac{V}{V_o}\right)^{a'-1} \qquad [12]$$

When one deals with the countercurrent flow, then -- just as in the case of the concurrent one -- the speed of the flow in the radial direction is equal to zero ($u = 0$). However, the value of the equalizing diffusion flow is commensurable with that of convection flow, and cannot in this case be neglected. In the case under discussion, the speed of the flow in the axial direction w is independent of the centrifuge height z. Taking these premises into consideration, one obtains, on the basis of the general equation [2], the following equation for the countercurrent flow:

$$p\frac{\partial N}{\partial t} = \frac{Dp}{r}\cdot\frac{\partial}{\partial r}\left[r\frac{\partial N}{\partial r} + 2\Delta A\cdot r^2 N(1 - N)\right] - pw\frac{\partial N}{\partial z} + Dp\frac{\partial^2 N}{\partial z^2} \qquad [13]$$

For the state set forth assuming that N 1, the solution to this equation supplies the ratio of the concentrations of the enriched isotope on either side of an ultracentrifuge of z height:

$$\frac{N_z}{N_o} = \frac{(1+\psi)e^{2ez(1+\psi)}}{(1+\psi)e^{2ez(1+\psi)}} \qquad [14]$$

In this equation:

$$\psi = \frac{PRT}{4\pi\cdot\Delta A\int_0^{r_2} r\cdot dr\int_0^{r} pwr\cdot dr}$$

and

$$e = \frac{\Delta A\int_0^{r_2} r\cdot dr\int_0^{r} pwr\cdot dr}{Dp\frac{r_2^2}{2}\quad\frac{1}{Dp}\int_0^{r_2}\frac{dr}{r}\left(\int_0^{r} pwr\cdot dr\right)^2}$$

The above expression is identical with the equation for enrichment in a split rectangular cascade. Further details and a wider elaboration of the subject can be found in Cohen's monograph mentioned above, and in the work by Martin and Kuhn (52).

It is also worth mentioning that, according to Martin and Kuhn, the rotor of a z length centrifuge, divided by means of parallel partitions into s sections so that $s = z/a$ (a -- width of the convection flow stream), will allow for a separation twice as important as a centrifuge of the same size not divided into compartments.

The problem of analogies between centrifugation and thermal-diffusion is not without importance for understanding the theory of centrifugation. As was said before, these analogies were mentioned in the very earliest period of theoretical research. Of later works, Bramley's (51) is worth mentioning; he stresses the great similarity of these two operations.

Such similarity is particularly pronounced when both operations are performed under optimum conditions, the pressure remaining unchanged, and the width of the convection flow stream also remaining so. Martin and Kuhn (52) described the problem in a more comprehensive way than other researchers.

The similarity of these operations is reflected in the formal analogy of a series of equations describing the two processes. For the simple effect of isotopic enrichment, Chapman (2) derives the following equations:

For thermal-diffusion $$\frac{\partial N}{\partial x} = -k_T \frac{\partial \ln T}{\partial x} \qquad [15]$$

For centrifugation $$\frac{\partial N}{\partial x} = -k_p \frac{\partial \ln P}{x} \qquad [16]$$

The value of coefficients in equations [15] and [16], when certain simplifying premises are applied, is equal to:

$$k_T \approx \frac{2}{3} \cdot \frac{M_1 - M_2}{M_1 + M_2} N \qquad [17]$$

and

$$k_p \approx \frac{M_1 - M_2}{M_2} N \qquad [18]$$

As can be seen by comparing the essential general equation for differential centrifugation [2] with the essential differential equation for thermal-diffusion [19]:

$$\varrho \frac{\partial N}{\partial t} = \frac{\partial}{\partial x} D \varrho \left[\frac{\partial N}{\partial x} - \frac{a}{T} \cdot \frac{\partial T}{\partial x} N(1 - N) \right] - \varrho w \frac{\partial N}{\partial z} + D \varrho \frac{\partial^2 N}{\partial z^2} \qquad [19]$$

Formal analogy occurs also in this case. (It must be borne in mind that pM/RT).

The essential difference between the two processes is illustrated by the expressions for the coefficient of separation. The coefficient for thermal diffusion:

$$\ln a_T = \frac{2}{3} \cdot \frac{M_1 - M_2}{M_1 + M_2} \ln \frac{T_g}{T_z} \qquad [20]$$

and for centrifugation:

$$\ln a_p = (M_1 - M_2) \frac{(\omega r)^2}{2RT} \qquad [21]$$

and, therefore, unlike the coefficient of isotope separation in centrifuging, the coefficient of separation through thermal-diffusion is in inverse proportion to the sum of molecular weights.

The theory of convection flow in a centrifuge worked out by Martin (48) should also be mentioned. Martin derives the following equation for the convection flow of the stream of gas between parallel walls, z being the distance between the walls:

$$\frac{\partial^4 w}{\partial z^4} - \frac{g \varrho_o}{\eta \lambda T_o} \cdot \frac{\partial p}{\partial r} w = 0 \qquad [22]$$

from which the expression is derived for the speed of the flow:

$$w = \frac{X}{2\varphi^2}(A\, e^{\varphi z}\cos\varphi z + B\, e^{-\varphi z}\cos\varphi z + C\, e^{\varphi z}\sin\varphi z \quad D\, e^{-\varphi z}\sin\varphi z \qquad [23]$$

In the above equation, A, B, D, and D are integration constants which can be computed for boundary conditions: $z = 0$, $z = a$, $T = T_1 = T_o + \Delta T$; however

$$x = \frac{g \varrho_o}{\eta T_o}\Delta T \qquad \text{and} \qquad \varphi = \frac{1}{2} \cdot \sqrt[4]{\frac{2 g \varrho_o}{\eta \lambda T_o}}$$

The volume speed of the flow is equal to

$$v = \int_0^a w \cdot dz \qquad [24]$$

and the value of w is supplied by equation [23].

After integrating, the author derives

$$v = \frac{X}{2\varphi^3}\,\Phi \qquad [25]$$

in which $\Phi = f(a)$, and $a = \varphi a$.

The function $\Phi = f(a)$ has features shown by the curve of the diagram. Fundtion Φ attains its maximum when $a = \pi$, and then slightly (by about 9%) decreases. Later on, its value is very close to one, and is independent of the value of a.

Accordingly, the volume speed of the flow dependent upon the distance separating the walls attains its maximum at

$$a_{opt} = \frac{\pi}{\varphi}$$

while after a slight decrease it remains steady. When the distance between the walls is short, $a \ll a_{opt}$ and $a \lll \pi$, then

$$v = \frac{g \varrho_o}{12\eta} \cdot \frac{\Delta T}{T_o}\, a^3$$

The course of function $\Phi = f(a)$.

Therefore, in this case the volume flow is proportional to the third power of the distance separating the walls.

No experimental data confirming the author's assertions are available at present.

General theoretical problems concerning the operation of centrifuging and the design of centrifuges can be found in, among others the works by Ciborowski (55) and Kasatkin (56) as well as the encyclopedic publications by Kirk and Othmer (57) and by Perry (59). The problems connected with the separation of gas mixtures are discussed by Chariton (60).

IV.

As mentioned above, experiments on the separation of isotopes in an ultracentrifuge were resumed after a lengthy interval, when the equipment difficulties had been surmounted and when ultracentrifuges had attained a relatively high degree of technical perfection.

Experiments concerning gas mixtures were the first to be resumed. They were conducted in 1936 by Beams and Haynes (25), designers of modern ultracentrifuges. The results agreed with the theoretical premises. Beams and Masket (26) also confirmed the theoretical forecase made by Mulliken, concerning the effectiveness of differential centrifugation in the case of tetrachlorure of carbon. The subsequent works by Beams and associates (27, 28) reconfirmed the previous results, and certain quantities (16 cu cm) of tetrachlorure of carbon were obtained, with its Cl^{37} content increased by 5%.

The results obtained corresponded with Mulliken's forecast in cases when a star-shaped partition was introduced in the rotor for the purpose of maintaining an even angular velocity of vapor throughout the rotor chamber. For, through taking off a part of vapor, one determines a certain flow of vapor from the periphery following an axial direction. When these inserts are not used, the vapor, maintaining its peripheral linear velocity, increases its angular velocity as it flows toward the center. Evidently, this phenomenon to a great extent invalidates Mulliken's theoretical premises.

Humphreys (29) subjected ethyl bromide to centrifugation in fields with a centrifugal force equal to 388,000 g. The Br^{79}: Br^{81} abundance ratio was modified by 11%. The results agreed with the theoretical forecasts calculated for a system the state whereof differed in a determined manner from that of equilibrium. Pollock (10) states that in centrifuging chloral hydrate in its temperature of condensation at the peripheral linear velocity equal to $5 \cdot 10^4$ cm/sec one obtains the value of the coefficient of separation equal to 1.25 instead of 1.11 as obtained at room temperature.

During World War II, very extensive research into the enrichment of U^{235} in an ultracentrifuge was conducted in the USA. However, this method was considered less convenient than the gas effusion one (58). No detailed data on such research were published.

After the war, a number of works on the separation of isotopes in an ultracentrifuge were published in the scientific literature of West Germany.

Beyerle and associates (41, 42) investigated the system of two ultracentrifuges, coupled by gas ducts. By using a suitable external contraption or otherwise through a cyclical modification of the rotational speed, an oscillating gas flow was brought about between the two ultracentrifuges. According to the authors, such gas was to favor the emergence of countercurrent. The ultracentrifuge rotors made of bondur (light metals) were 120 mm in diameter and 400 mm in length. They were driven by an asynchronous, 60,000 r.p.m. electric motor. The rotor of the motor and that of the ultracentrifuge were coupled by means of a steel capillary.

In certain series of experiments, several inserts, parallel to the bottom cap of the chamber were used. They divided the chamber into a number of parallel compartments. The work does not include detailed data for a critical evaluation of the purposefulness of the use of a system of twin ultracentrifuges and of partitions in their chambers.

In centrifuging hexafluoride of uranium in an ultracentrifuge without partitions, the authors obtained the results shown in Table 2:

Table 2

Speed in r.p.m.	25,000	30,000	40,000	45,000	50,000
Coefficient of separation	1.012	1.020	1,036	1.047	1.058
Efficiency in g/h	2.3	1.6	0.85	0.70	0.57

In certain series of experiments, to the isotopic mixture under separation, the authors added hydrogen up to 90%. It was supposed that the hydrogen would eliminate the thermal effects brought about by the Martin radial convection currents. Due to the light atomic weight of hydrogen, even in extreme cases the ratio of pressures in the peripheral and central parts of the rotor should not have exceeded 1.04, and the thermal effects connected with the compression and the decompression of gas would have had to be slight. In such cases, the separation effects were believed to improve. The authors' anticipations failed to materialize in a clear-cut manner. There were a number of results which did not repeat themselves, and often contradicted one another.

The influence of hydrogen addition on the separation effect was investigated in several other works. Groth and Harteck (40), co-authors of the work referred to above investigated such influence upon the differential separation of krypton and selenium isotopes in an ultracentrifuge. In addition to the problems discussed in the work referred to above, the authors explain the advantages of hydrogen addition by its

high thermal conductivity which causes rapid disappearance of temperature gradients inside the rotor and, thereby, the disappearance of harmful convection currents. Apart from findings matching Humphreys' reasoning referred to earlier, the materials contained in the work do not warrant any positive conclusions with regard to the "stabilizing" -- the authors' own term -- properties of hydrogen.

In similar manner, the influence of hydrogen was left unexplained in the work by Faltings, Groth, and Harteck (43) on the separation of xenon isotopes in a mixture with hydrogen. Among other features, the authors, trying to combine the effects of rotation with those of thermal-diffusion, introduced in the rotor a length of steel wire (which did not rotate with the rotor), and had current flow through it. As it occurred, in such cases all separation effects disappeared whether or not the current was flowing through the wire. The authors surmise that probably the vibrations of the wire checked the separation of the isotopic mixture.

In the same work, the authors obtained a sizeable augmentation of the separation effect by placing a heating element at the bottom end of the centrifuge. Under optimum conditions, they obtained a 1.5 value of the coefficient of separation. At excessively high temperatures, the separation effect decreased. This circumstance argues in favor of a certain optimum convection flow as foreseen by Martin and Kuhn.

Going back to hhe problem of the "stabilizing" properties of hydrogen added, it would appear from the work by Faltings and Seehofer (44) concerning the separation of germanium isotopes that the favorable influence of hydrogen on the separation effect has been proved, qualitatively at least. When rotating germanium-hydrogen in a 124 mm diameter centrifuge, 700 mm high at 40,000 r.p.m. in a 70% hydrogen mole mixture, the authors obtained an increase in the separation coefficient which became twice (1.2 instead of 1.09) as high as the theoretical one. However, an attempt to reconstitute such results, undertaken by Hertz and Nann (45, 46), resulted in failure. The separation effect was even lower than the theoretical one.

The same authors state that in centrifuging xenon they obtained the following values of the coefficient: 1.47 - 1.63, and so 4 to $5\frac{1}{2}$ times higher than the theoretical one in cases when an isotopic mixture in the 12 - 50 cu cm/min range was flowing at stabilized speed through the rotor.

One of the very important conclusions of the work referred to is the fact that in the countercurrent separation of isotopes in a centrifuge, fractions with varying contents of a component under investigation pile up at both ends of the rotor, and that the location of the point where the samples are collected (whether at the axial or peripheral portion of the rotor chamber) does not affect their composition. The promising results of this work brought about attempts to separate hexafluoride of uranium during its flow at steady speed through the rotor chamber. The degree of enrichment rose to a certain maximum as the difference increased between the temperature of the top and that of

the bottom portion of the centrifuge, and then began to drop. When the direction of the axial gradient of temperature was reversed, the location of the spot where the enriched fraction (s) gathered, shifted as well.

The theoretical value of the coefficient of separation, calculated on the basis of Martin and Kuhn's theory, amounted to 1,185 for the experiment's conditions (cenyrifuge diameter -- 134 mm, length -- 635 mm, linear peripheral velocity -- 250 m/sec). In experiments, the value was found to be 1,190.

A very important development which favorably distinguishes the centrifugation method was the fact that the time of relaxation of the system proved to be very short. In the experiment referred to, it amounted to no more than 12 minutes. On these grounds, the authors calculate the efficiency of the centrifuge with 300 m/sec peripheral velocity, 635 mm long at 155 Kg/year of uranium enriched by 60% of its initial U^{235} content.

The results obtained are so promising that the possibility of industrial use of the method of uranium enrichment in an ultracentrifuge is being seriously discussed in the professional literature of certain countries (61).

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Symbols

- a — distance between parallel walls or partitions of centrifuge
- D — coefficient of diffusion
- e — basis of natural logarithms
- g — relative gravitational momentum, unit of tension of centrifugal force field
- L — molar speed of flow
- M — molecular weight
- N — molar fraction
- N_o — molar fraction of component undergoing separation, at the entrance to the centrifuge
- N_z — molar fraction of component undergoing separation, at the exit from the centrifuge
- p — pressure
- P — molar speed of flow
- R — gas constant
- r — distance from axis of centrifuge
- t — time
- T — absolute temperature
- T_o — absolute temperature of environment
- T_1 — absolute temperature of walls
- ΔT — difference between temperature of centrifuge and that of environment
- T_z — absolute temperature of wall when cold
- T_g — absolute temperature of wall when hot

u linear speed of the radial flow
w linear speed of axial flow
v volume speed of flow
V_o initial volume in differential centrifuging
V final volume in differential centrifuging
x distance in the direction of x axis (direction correlate with that of centrifuge radius)
z distance in the direction of z axis, length of centrifuge, distance between parallel walls or partitions of centrifuge
a_o coefficient of separation of simple isotopic effect
a' coefficient of isotope separation, characteristic for multiple system of separation
η coefficient of viscosity
λ coefficient of thermal inductiveness
ρ density
ω angular velocity

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